A generic platform for the visualization of all monomer sequences in individual copolymer chains

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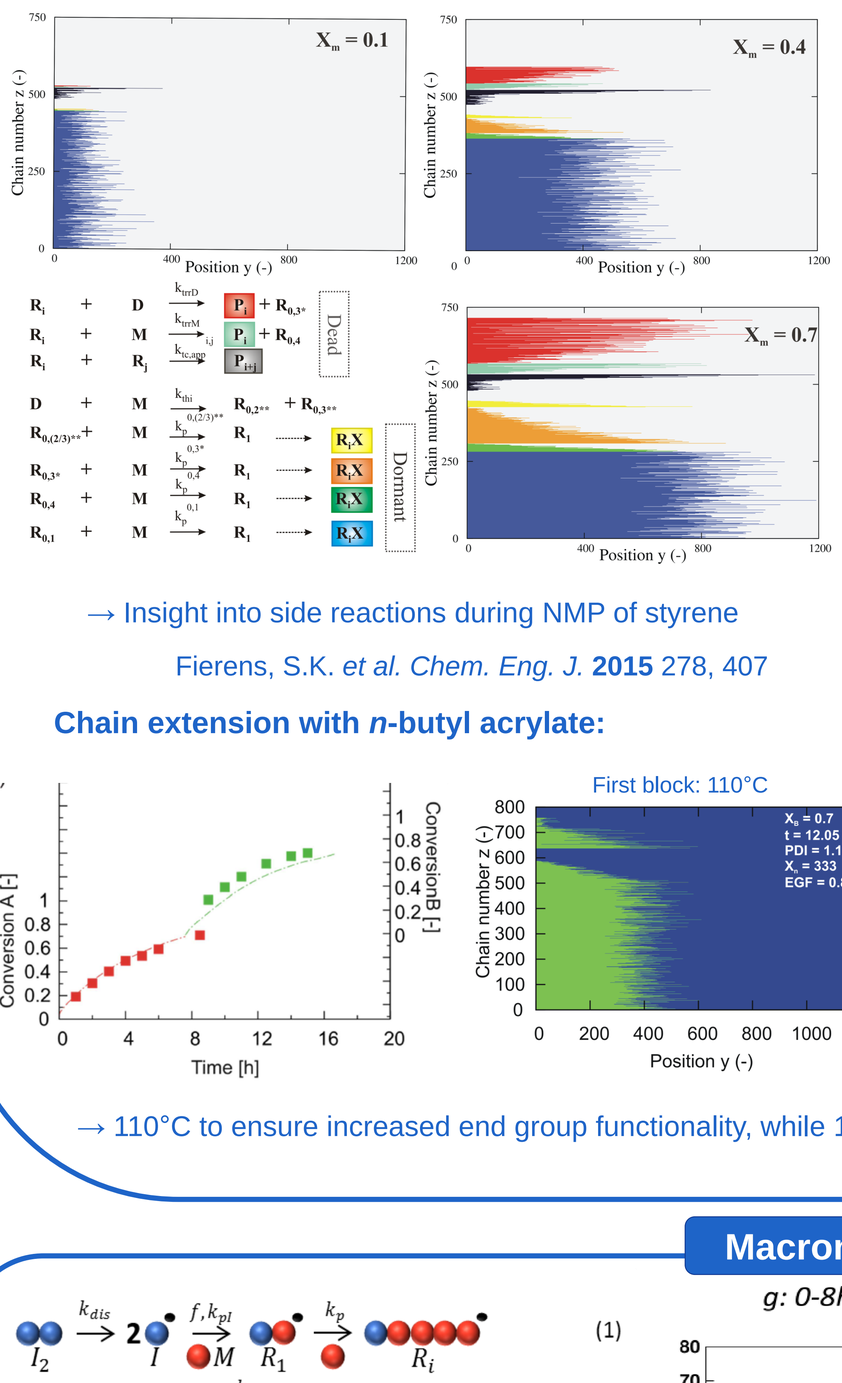
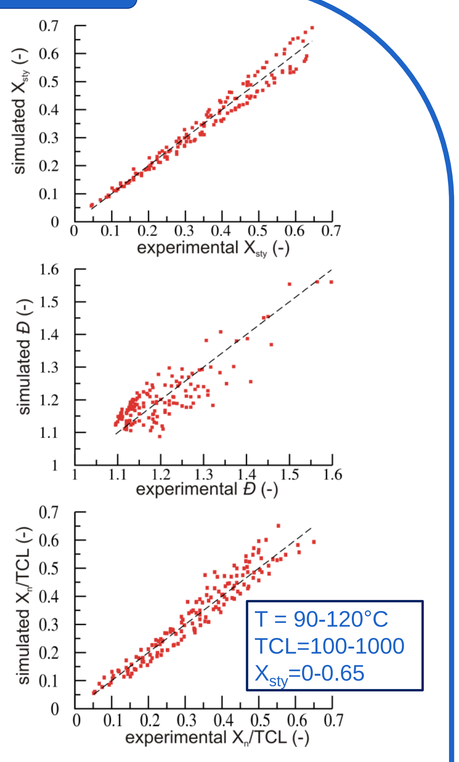
INTRODUCTION

One of the key challenges for future polymer synthesis is the detailed characterization of individual macrospecies, including the position of all monomer units and functionalities. In this contribution, it is demonstrated that advanced modeling techniques in combination with detailed experimental procedures allow to overcome this challenge. These techniques are further used to identify the most suited protocols for the synthesis of advanced macromolecular architectures, accounting for the possible impact of diffusional limitations and side reactions. Examples are included both for radical and cationic processes. The presented modeling platform is generic and can lead to a significant progress in the field of macromolecular engineering.

NITROXIDE MEDIATED POLYMERIZATION

Estimation of NMP specific Arrhenius parameters





→ Insight into side reactions during NMP of styrene

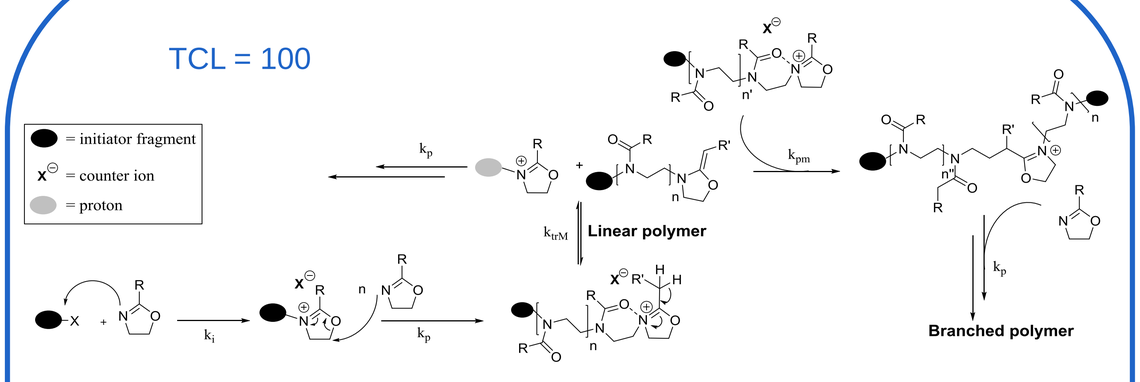
Fierens, S.K. *et al. Chem. Eng. J.* **2015** 278, 407

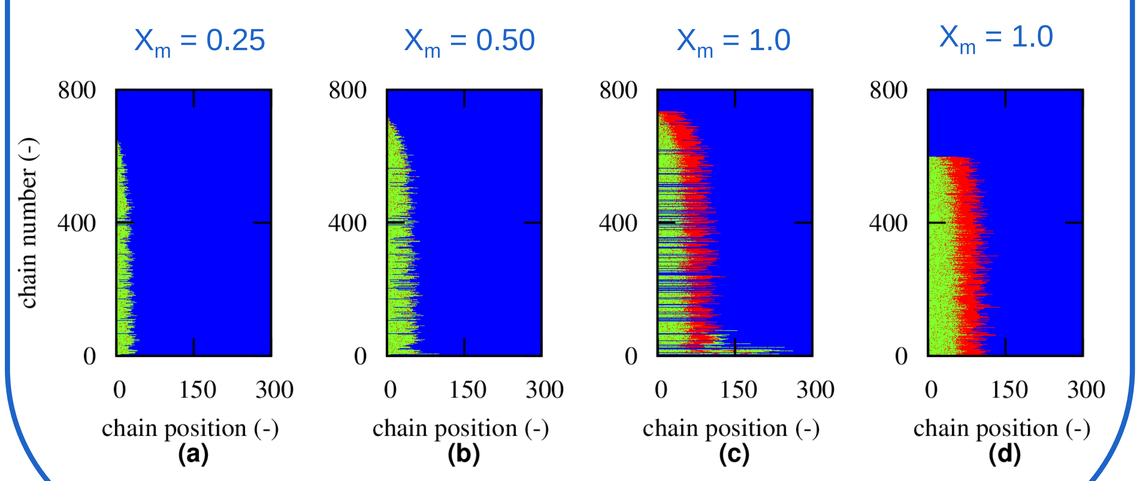
TCL = $[STY]_0/[MAMA\text{-}SG1]_0$

Chain extension with *n*-butyl acrylate:

→ 110°C to ensure increased end group functionality, while 130°C ensure low reaction time

CATIONIC RING OPENING POLYMERIZATION

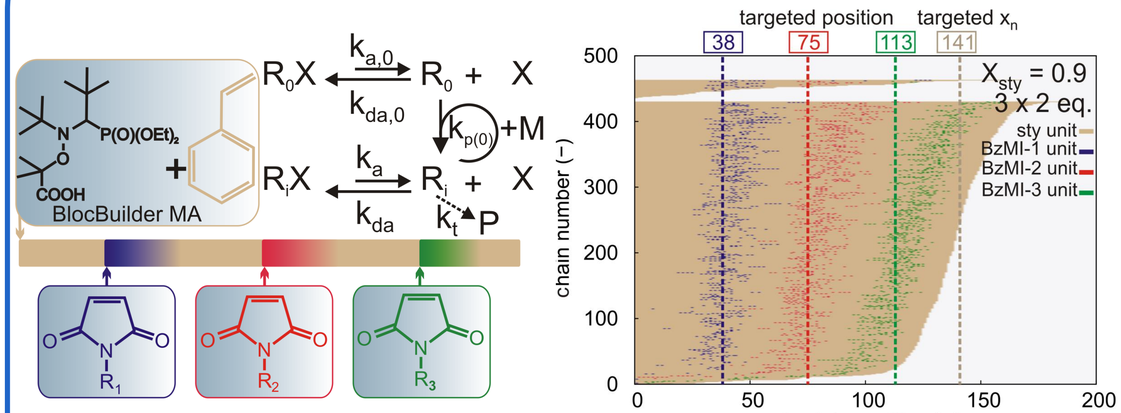




→ Differentiation between homopolymer, gradient and branched chains

SEQUENCE-CONTROLLED COPOLYMERS

- Combination of e^--donor and e^--acceptor monomers
- *In silico* synthesis of a trifunctionalized copolymer

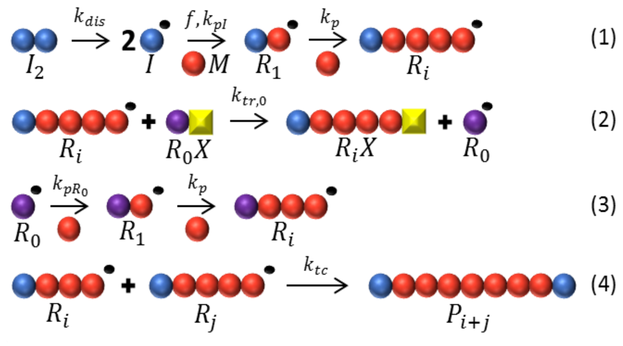


T=120°C $[Sty]_0$:$[R_0X]_0$:$[BzMI\text{-}1]_{AP1}$:$[Sty]_{AP2}$:$[BzMI\text{-}2]_{AP3}$:$[Sty]_{AP4}$:$[BzMI\text{-}3]_{AP5}$:$[Sty]_{AP6}$ =47:1:eq.:45:eq.:45:eq.:13

Zamfir, M. and Lutz, J.-F., *Nat. Commun*. **2012**, 3, 1138

Fierens, S.K. *et al.*, *Macromolecules* **2016,** 49, 9336

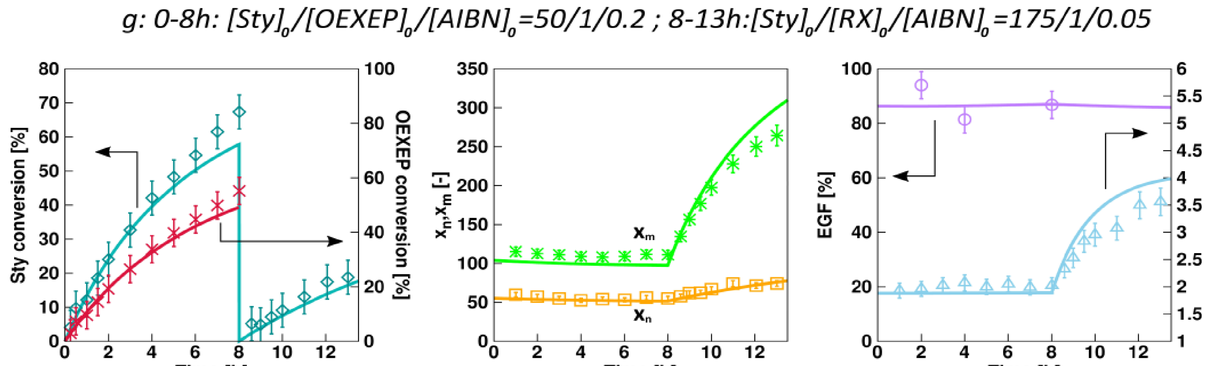
Macromolecular design via the interchange of xanthates



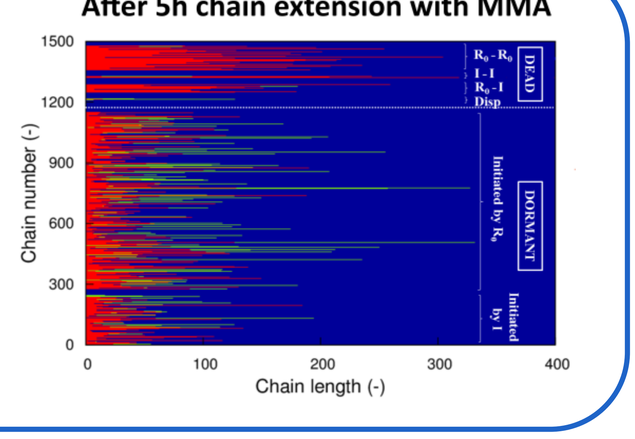
→ 1 exchange cycle per dormant chain

→ estimation of $C_{tr,(0)}$

g: 0-8h: $[Sty]_0/[OEXEP]_0/[AIBN]_0$=50/1/0.2 ; 8-13h:$[Sty]_0/[RX]_0/[AIBN]_0$=175/1/0.05



D.J.G. Devlaminck *et al.* **2017** *Polym. Chem*. submitted



CONCLUSIONS

- A generic platform is developed for polymer design accounting for side reactions and diffusional limitations
- Visualization of all monomer sequences is possible using a kinetic Monte Carlo algorithm, recording every reaction event an individual growing polymer molecule undergoes.
- Insight into the mechanisms behind chain-to-chain deviations.
- Experimental validation whenever possible, combined with model-based design via selection of agents and reaction conditions.

ACKNOWLEDGMENTS

This work is supported by the Long Term Structural Methusalem Funding by the Flemish Government, the Fund for Scientific Research Flanders (FWO) and the Interuniversity Attraction Poles Programme P7/5 - Belgian State – Belgian Science Policy are acknowledged for financial support.

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12th International Conference on Advanced Polymers via Macromolecular Engineering (APME 2017), Ghent, 21-25/05/2017